Novel Heterocumulenes: Bisiminopropadienes and Linear Ketenimines

Reinhard Wolf, Stefan Stadtmüller, Ming Wah Wong, Monique Barbieux-Flammang, Robert Flammang, and Curt Wentrup*

Abstract: Flash vacuum thermolysis (FVT) of suitably substituted isoxazol-5(4*H*)-ones **7–9** leads to three different types of ketenimines, namely, the isoxazolonoketenimines **2**, the novel bisiminopropadienes RN=C=C=C=NR (**5**), and the *C*-cyanoketenimines **14**, all characterized by a combination of FVT/matrix isolation/IR spectroscopy and FVT/MS. An unusual, linear C=C=N–C backbone in ketenimines **2g** and **2h** is revealed by their exceptional spectroscopic properties as well as an X-ray crystal structure of **2g**, and confirmed by density functional calculations (B3LYP/6-31G*); these compounds are best described as resonance hybrids of ketenimines and isonitrile ylides $R_2\bar{C}-C\equiv\overset{+}{N}-R'$. The identification of the highly reactive bisiminopropadienes **5** is supported by the observed shifts in the IR bands of the ^{15}N and ^{13}C isotopomers as well as theoretical calculations. *tert*-Butyl-substituted isoxazolones **7e** and **7f**, and **8i** form the expected ketenimines **2**, which then undergo elimination of isobutene and CO_2 to generate *C*-cyanoketenimines **14** and **14i**. *N*-Phenyldicyanoketenimine **32** is also described.

Keywords
cumulenes · heterocumulenes · ketenimines · matrix isolation · thermolysis

Introduction

Owing to their high reactivity, only a small number of compounds with more than two cumulated double bonds were know until recently. The earliest example of a heterocumulene C_nX_2 ($n>1$) was Otto Diels' carbon suboxide, C_3O_2 (O=C=C=C=O), reported in 1906.[1a] The homologous dithione S=C=C=C=S has an even longer history although it is less well known,[1b] and C_3OS is a relatively recent addition.[1c]

Mass spectrometric and matrix isolation techniques have allowed the synthesis and characterization of a large number of C_nS_2, C_nOS, and C_nO_2 species.[2] Some of these newly discovered heterocumulenes are surprisingly stable. C_5O_2 (O=C=C=C=C=C=O) is stable in solution at room temperature;[2d] the sulfur analogue C_5S_2 is stable in dilute solution below $-30\,^{\circ}C$.[2e] In general, heterocumulenes with odd numbers of cumulated atoms prove to be more stable than the ones with an even number. The most elusive species in this series are undoubtedly the C_2X_2 compounds. Ethenedithione (S=C=C=S) was identified by Sülzle and Schwarz, Maier et al., and our group by means of neutralization–reionization mass spectrometry (NRMS), flash vacuum thermolysis (FVT), and matrix isolation techniques.[3] Both O=C=C=S and RN=C=C=S were identified by NRMS.[4] Ethenedione, O=C=C=O, the formal dimer of carbon monoxide, is still unknown, but the matrix isolation of its monoxime (HON=C=C=O) was reported recently.[5] Oxygen and sulfur are of course not the only heteroatoms of interest. We reported the first synthesis of iminopropadienones (RN=C=C=C=O) in 1992.[6] NRMS evidence for the existence of the parent iminopropadienone (R = H) and the mono- and disubstituted bisiminopropadienes (RN=C=C=C=NR) has been presented,[7] but, as expected, the *NH* compounds undergo facile tautomerization to cyanoketene (NC–CH=C=O) and malodinitrile (NC–CH_2–CN) under FVT conditions.[7a,b]

Here, we report full details of our investigation of the use of isoxazolones of the type **1** as thermal precursors of bisiminopropadienes, RNC_3NR (**5**) (Scheme 1).[8] The rationale for this approach is the observation that ketene *S,N*- and *N,N*-acetal (aminal) derivatives of isoxazolone (**1**, X = SCH_3 or NR_2) undergo facile elimination of methanethiol or dialkylamine under FVT conditions. Analogously substituted Meldrum's acid derivatives react in the same manner.[6,9] In both cases, a transient ketenimine is the expected primary product, but such a compound (**2**) has not previously been observed in the isoxazolone series.[8]

Cleavage of the N–O bond and elimination of CO_2 is the standard fragmentation of isoxazolones.[9,10] This would convert **2** to the nitrene **3**,[11] which could either cyclize to azirine **4** or undergo a direct 1,2-shift of the group R to generate the desired bisiminopropadiene **5**.

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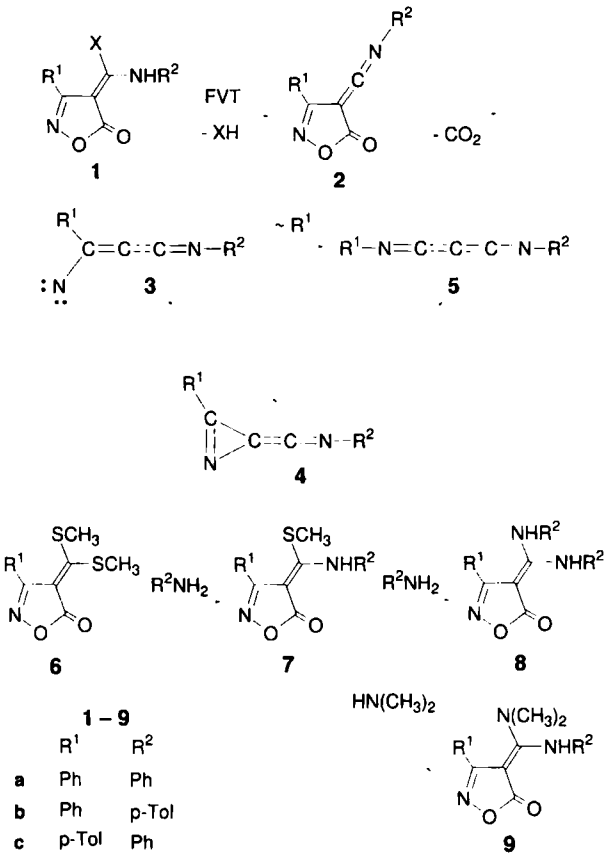
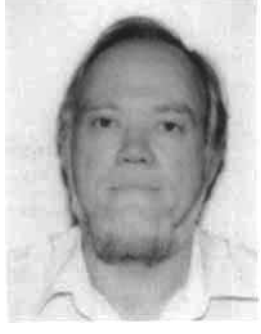


	R^1	R^2
a	Ph	Ph
b	Ph	p-Tol
c	p-Tol	Ph
d	p-Tol	p-Tol
e	t-Bu	Ph
f	Ph	t-Bu
g	t-Bu	2,4,6-tri-*tert*-butylphenyl
h	Ph	2,4,6-tri-*tert*-butylphenyl
i	t-Bu	2-*tert*-butylphenyl
j	CH_3	Ph
k	CH_3	p-Tol
m	Ph	CH_3

Scheme 1.



Editorial Board Member:[*] *Curt Wentrup was born and raised in Denmark, studied at Kobenhavns Universitet (cand. scient. 1966), moved to Australia out of curiosity, and obtained a PhD from the ANU (Canberra, 1969) followed by a Dr. Scient. from Kobenhavns Universitet. He has held posts at the Université de Lausanne and the Universität Marburg, and is now at the The University of Queensland (since 1985). He is interested in new reactive molecules, new synthetic methods, and techniques for generating and investigating those molelcules. He collaborates closely with Robert Flammang at the Université de Mons on the application of advanced mass spectrometry methods in the investigation of reactive intermediates.*

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Results and Discussion

Synthesis of Starting Materials: 3-Substituted isoxazol-5(4*H*)-ones are usually prepared from alkanoyl- or aroylacetoacetates with hydroxylamine hydrochloride.[12] The required ketene dithioketals **6** (Scheme 1) were obtained by deprotonation at C-4, coupling with CS_2, and alkylation with CH_3I[3c, 4b] in analogy with similar procedures for Meldrum's acid derivatives.[13] Stepwise exchange of the methylthio substituents in **6** gave access to a wide variety of derivatives **7** and **8**. The first methylthio substituent was usually easily replaced by amines at ambient temperature. Replacement of the second methylthio substituent often required longer time, higher temperatures, or catalysis with $HgO/HgCl_2$.[14] However, for 3-*tert*-butylisoxazolone **6e**, the first step had a substantial activation energy, whereas the second step proceeded smoothly under the same conditions to give **8**. Hence, it was difficult to obtain monosubstituted 3-*tert*-butyl-**7**, except for **7e**, which was obtained by reaction of **6e** with aniline at room temperature, and for **7g**, where the sterically demanding 2,4,6-tri-*tert*-butylphenylamino substituent could only be introduced by deprotonation of the aniline with butyllithium. This was also required for the synthesis of **7h**. Disubstitution to **8e,g,h** did not occur. 3-Methylisoxazolone derivatives **6–9j,k** were easily synthesized by the standard procedures.

In all cases, we obtained only one stereoisomer of **7**, **8**, and **9**. Although we do not know whether these compounds are (*Z*) or (*E*) with respect to the exocyclic double bond at C-4, we assume that the stereospecificity may be due to H-bonding to the carbonyl group at C-5 in **7** guiding the first amine substituent into the (*Z*) configuration.

Attempts to synthesize isoxazolones with mesityl or 2,4,6-tri-*tert*-butylphenyl substituents in position 3 were unsuccessful. Ethyl mesitoylacetate did not give an isoxazolone on treatment with hydroxylamine hydrochloride. 2,4,6-Tri-*tert*-butylacetophenone gave only a trace of the corresponding aroylacetoacetate on reaction with diethyl carbonate.

Flash Vacuum Thermolysis (FVT) Experiments:

1. 3-Aryl-Substituted Isoxazolones 7/9a–d: As we have shown previously, aryl substituents are able to stabilize cumulenic structures such as iminopropadienones more effectively than alkyl substituents.[6] The first compound to be investigated as a precursor of a bisketenimine **5** was therefore isoxazolone **7a**. At FVT temperatures of 300 to 650 °C a number of IR absorptions different from the starting material appeared in the spectrum of the Ar matrix isolated product (Fig. 1a). The most prominent ones are at ca. 2099, 2075, and 1772 cm^{-1}. Absorptions due to methanethiol are also present,[15] and in certain experiments at high temperatures bands due to benzonitrile and phenyl isocyanate appear. The latter two compounds are due to side reactions involving the breakdown of the isoxazolone ring; we found that their formation can be almost totally suppressed by using very gentle sublimation conditions in the FVT apparatus. We suspect that the formation of benzonitrile and phenyl isocyanate takes place in the solid state at temperatures close to the melting point of the starting material. Temperatures of almost 200 °C had to be employed to achieve an adequate rate of sublimation at a vacuum of approximately 10^{-5} mbar. The isoxazolones **7/9** usually melt with gas evolution and tar formation.

The compound absorbing near 2100 and 1772 cm^{-1} is formed from **7a** by loss of methanethiol. There is not yet any significant *increase* in the intensity of the CO_2 absorptions at 2340 and 2345 cm^{-1}. The prominent CO_2 signal in Fig. 1a is due to the

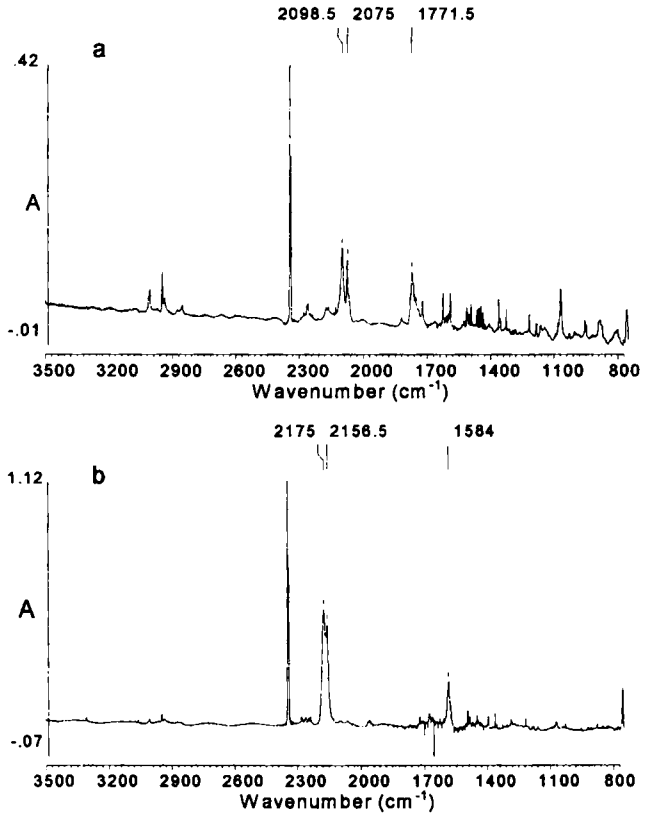


Fig. 1. IR spectra of the products of FVT of **7a**, a) at 650 °C giving **2a**; b) at 850 °C giving **5a** (Ar, 12 K).

unavoidable decomposition of the starting material in the sublimation zone. It is reasonable, therefore, to assign the signals at ca. 2100/1772 cm^{-1} to isoxazolonoketenimine **2a** (Scheme 1).

A strong *increase* in the intensity of the CO_2 absorptions is observed when the FVT temperature is raised gradually to ca. 850 °C. A slow, synchronous disappearance of the signals at 2099, 2075, and 1772 cm^{-1} takes place. Simultaneously, a very strong, broad absorption at an average wavenumber of 2167 cm^{-1} appears. The spectrum eventually simplifies to one with only two major absorptions at 2167 (center) cm^{-1} and 1584 cm^{-1} (Fig. 1b). Further increase of the FVT temperatures up to 1000 °C did not lead to any significant change in the spectrum.

The high-temperature species is interpreted as being the bisketenimine **5a**: it is formed by extrusion of CO_2; it absorbs very strongly around 2167 cm^{-1} (antisymmetric stretch) in agreement with our theoretical calculations (vide infra); it has a mass of 218 (vide infra); and exactly the same IR spectrum is also obtained by FVT of **9a**. The shape of the very broad IR signal (Fig. 1b) cannot be improved by modification of deposition parameters and therefore has to be interpreted as being due to either a persistent matrix site effect or an intrinsic effect of the substituents.

The formation of **5a** from both **7a** and **9a** was confirmed by FVT/MS experiments. The precursor molecules eliminated CH_3SH and $HNMe_2$, respectively, at between 350 and 400 °C. The resulting ions (m/z = 263), corresponding to the isoxazolonoketenimine **2a**, reached their maximum intensity at 650 °C. The spectrum of these ions is shown in Fig. 2a. From 500 °C onwards, ions of m/z = 218 started appearing in the spectra, corresponding to loss of CO_2 from **2a**. The collisional activation (CA) mass spectra of these m/z = 218 ions changed as a function of temperature. The final product, obtained at 800 °C, corresponds to PhN=C=C=C=NPh (**5a**) (Fig. 2b) in accord with the IR experiment (Fig. 1b). A slightly different CAMS obtained at 700 °C could be due to the formation of the azirine intermediate **4a** or (more likely) a mixture of **4a** and **5a**. The amount of **4a** formed is too small and the temperature range too narrow for its secure IR spectroscopic detection. It should be noted that the molecular ions of pyrimidine derivatives **10** undergo unimolecular decomposition to produce bisiminopropadiene ions $5^{\bullet+}$.[7c] The CAMS of $5a^{\bullet+}$ generated in this manner was identical with the one shown in Fig. 2b.

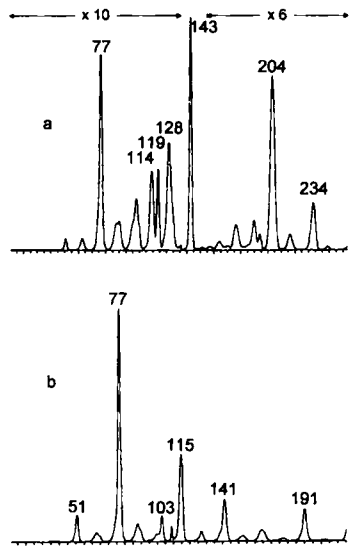
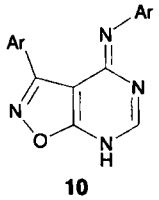
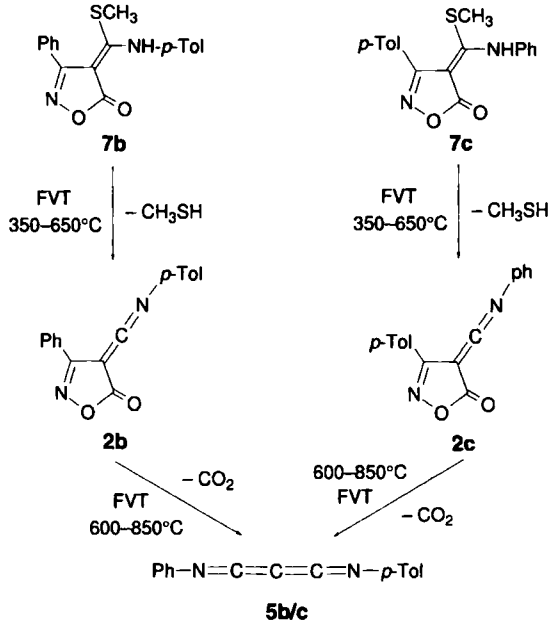


Fig. 2. FVT-MS of **7a**, a) CAMS(O_2) of the m/z = 263 ions ($2a^{\bullet+}$) formed at 650 °C; b) CAMS(O_2) of the m/z = 218 ions ($5a^{\bullet+}$) formed at 750–800 °C.



10

The isomeric precursors **7b,c** were investigated in order to demonstrate that the final product, the bisketenimine **5b/c**, does in fact have the proposed symmetrical structure (Scheme 2). FVT of **7b** and **7c** is expected to lead initially to two different isoxazolonoketenimines **2b** and **2c**, which can indeed be seen in the matrix IR spectra (Fig. 3a–b). Ketenimine absorptions due to **2b** appear at 2108, 2094, and 2079 cm^{-1}, whereas the absorptions of **2c** are slightly different (by ca. 10 cm^{-1}) at 2098, 2079, and 2072 cm^{-1}. Further increase in the FVT temperatures to ca. 800 °C should eventually lead to the bisketenimine **5b/c**. This is exactly what we observe: at temperatures above 650 °C the signals for the isoxazolonoketenimine **2b,c** start to decrease in intensity and in both cases a new, strong absorption at



Scheme 2.

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2167 cm^{-1} appears. The shape of this signal is exactly the same in both cases. The second major absorption at 1595 cm^{-1} is also due to an antisymmetric stretch of the cumulene (see labeling results below and Section 7). These identical IR spectra (Fig. 3c–d) are ascribed to **5b/c**.

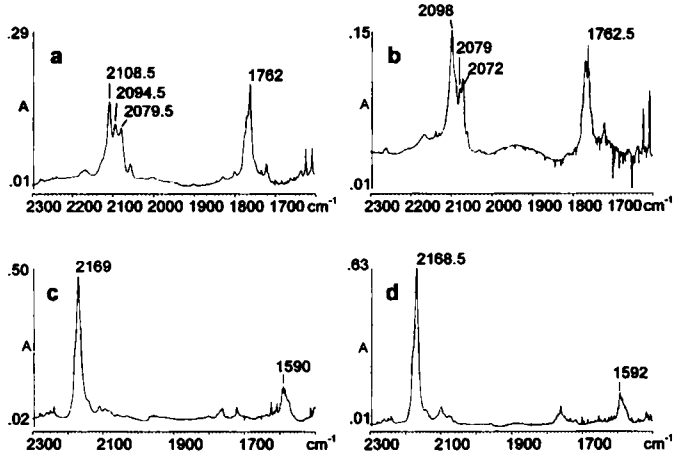


Fig. 3. Excerpts of IR spectra from FVT of **7b** and **7c** in an Ar matrix: a) **7b** at 650 °C (giving **2b**); b) **7c** at 650 °C (giving **2c**); c) **7b** at 800 °C (giving **5b/c**); d) **7c** at 800 °C (giving **5b/c**).

Again, the IR observations were corroborrated by FVT/MS experiments. Between 300 and 400 °C **7b** and **7c** eliminate MeSH to give ions with $m/z = 276$, corresponding to **2b** and **2c**. The CAMS of these two species are different; their main decomposition channels are the formation of Ph–N=C=C=C=O$^{\bullet+}$ and *p*-Tol–N=C=C=C=O$^{\bullet+}$, respectively. At 700–800 °C, thermal loss of CO_2 takes place, and mixtures of ions are formed from both precursors, corresponding to mixtures of azirines **4b,c** and bisiminopropadienes **5b,c** ($m/z = 232$). Above 800 °C, the CAMS of the $m/z = 232$ ions generated from **7b** and **7c** become identical with each other and with the CAMS resulting from unimolecular decomposition of the molecular ions of **10**.

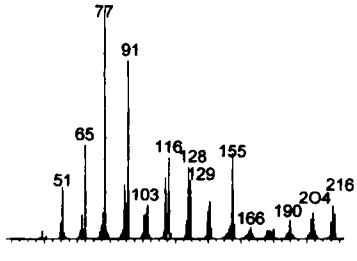


Fig. 4 Resolved CAMS(O_2) of the $m/z = 232$ ions (**5b/c**$^{\bullet+}$) from FVT of **7c** at $T > 800$ °C. The peaks at $m/z = 217$, 205, 129, and 91 are due to unimolecular decomposition as they are observed also in the absence of a collision gas. A nearly identical spectrum is obtained from **7b**.

The fragmentation pattern of these $m/z = 232$ ions is in accord with the structure of **5b/c** ($m/z = 115$: PhNCC; 129: *p*-Tol–NCC; 128 is formed from 129 by loss of H; 116 is due to M^{2+} (charge stripping)) (Fig. 4).

To complete this series of precursors, the doubly *p*-tolyl-substituted isoxazolone **7d** was examined. As expected, absorptions appear at 2100 and 1700 cm^{-1} at low pyrolysis temperatures and then vanish at higher pyrolysis temperatures. In this case, a very strong and sharp absorption at 2174 cm^{-1} appears at ca. 800 °C, which we again assign to the antisymmetric stretching vibration of the cumulene moiety in **5d** (Fig. 5).

In order to further corroborate the IR assignments of bisiminopropadienes **5**, we synthesized the ^{15}N- and ^{13}C-labeled precursor molecules **11** and **13** (Scheme 3) from ^{15}N-aniline and $^{13}CS_2$, respectively, by using standard procedures for

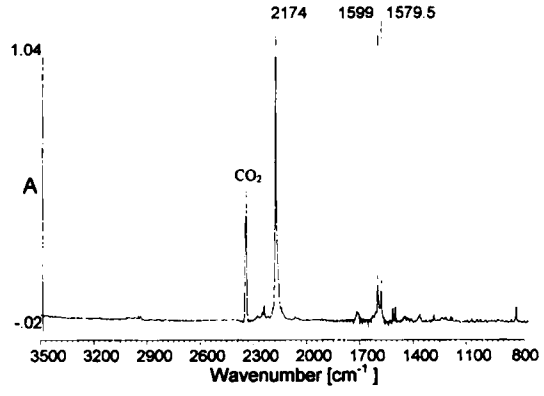
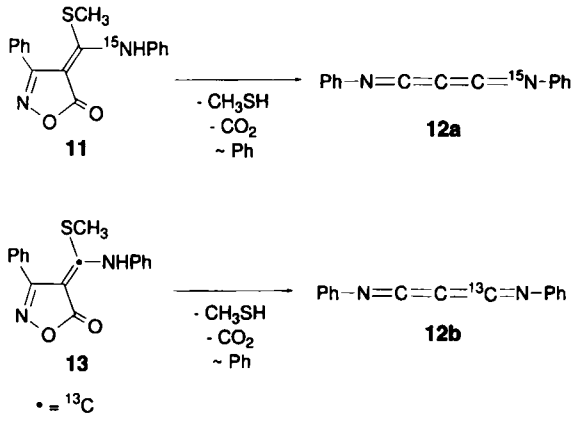


Fig. 5. IR spectrum of the product (**5d**) of FVT of **7d** at 810 °C (Ar, 12 K).



Scheme 3.

isoxazolone preparation. Density functional calculations predict a very small effect of ^{15}N, but a substantial effect of ^{13}C on the major cumulene absorption in the 2200 cm^{-1} region for various bisiminopropadienes (Table 1). The FVT of **11** and **13** at 800 °C gave cumulenes **12a** and **12b** with shifts of 0 and 18 cm^{-1} towards lower wavenumbers, respectively, in excellent accord with the theoretical predictions. The corresponding shifts of the 1582 cm^{-1} band were 13 and 1 cm^{-1} for **12a** and **12b**, respectively (calculated: 12 and 2 cm^{-1}, respectively) (Table 1).

In all the reactions of **7** outlined above, **9** gives identical results (Scheme 1). The elimination of dimethylamine from **9** takes place under milder conditions than the loss of methanethiol from **7** (cf. the iminopropadienones[6a]). However, the aminals **9** are more difficult to sublime, and they are prone to hydrolysis. Therefore, most experiments were carried out with derivatives of **7**.

The conclusion from this section is that ketenimines **2** and bisiminopropadienes **5** are formed in relatively clean reactions. However, neither is isolable at ordinary temperatures, and attempts to obtain NMR spectra of **5a–d** or to trap these compounds with nucleophiles failed. For this purpose, the products of a pyrolysis on a millimol scale were trapped on a liquid N_2 cold finger, which was then coated with a low-melting deuterated solvent. Upon evaporation of the liquid N_2, the reaction products warmed up until the solvent melted, and product and solvent flowed into an attached NMR tube, which itself was immersed in liquid N_2. In trapping experiments with nucleophiles (MeOH, Me_2NH), several products were formed upon melting of the solutions. These then reacted further when warmed up to give highly complex mixtures of products. The best solvent was CD_2Cl_2 for which temperatures down to

Table 1. Calculated vibrational frequencies (cm^{-1}) and IR intensities ($km\,mol^{-1}$) of substituted bisiminopropadienes ($R^1NCCCNR^2$) (**5**) and their isotopomers [a].

R^1	R^2	Mode	Frequency [b,c]			IR intensity [d]		
			$R^1NCCCNR^2$	$R^1N^{13}CCCNR^2$	$R^{1\,15}NCCCNR^2$	$R^1NCCCNR^2$	$R^1N^{13}CCCNR_2$	$R^{1\,15}NCCCNR^2$
H	H	ν_1	2207	−19	−2	2272	2176	2253
		ν_2	2022	−33	−7	0	28	0
		ν_3	1482	−3	−11	152	160	149
CH_3	H	ν_1	2203	−21	−3	2785	2658	2751
		ν_2	2043	−31	−11	0	52	1
		ν_3	1534	−1	−15	204	209	206
CH_3	CH_3	ν_1	2196	−19	−2	3360	3192	3320
		ν_2	2056	−32	−10	0	73	2
		ν_3	1579	−2	−14	274	287	275
CH_2=CH	H	ν_1	2192	−19	−2	3306	3151	3269
		ν_2	2028	−33	−10	1	66	2
		ν_3	1530	−1	−16	224	235	257
CH_2=CH	CH_2=CH	ν_1	2178	−18	−2	5028	4776	4967
		ν_2	2035	−32	−9	0	99	1
		ν_3	1568	−1	−12	119	151	258
C_6H_5	H	ν_1	2187	−18	−2	3739	3561	3697
		ν_2	2027	−34	−10	2	82	4
		ν_3	1536	−1	−17	432	447	440
C_6H_5	C_6H_5	ν_1	2166	−18	−2	6609	6260	6530
		ν_2	2034	−32	−10	0	153	2
		ν_3	1579	−2	−12	701	690	238

[a] B3LYP/6-31G* values. [b] Scaled by 0.945 (see text). [c] Isotopomer shifts for $R^1N^{13}CCCNR^2$ and $R^{1\,15}NCCCNR^2$. [d] The IR-forbidden vibrations are allowed in the Raman and vice versa.

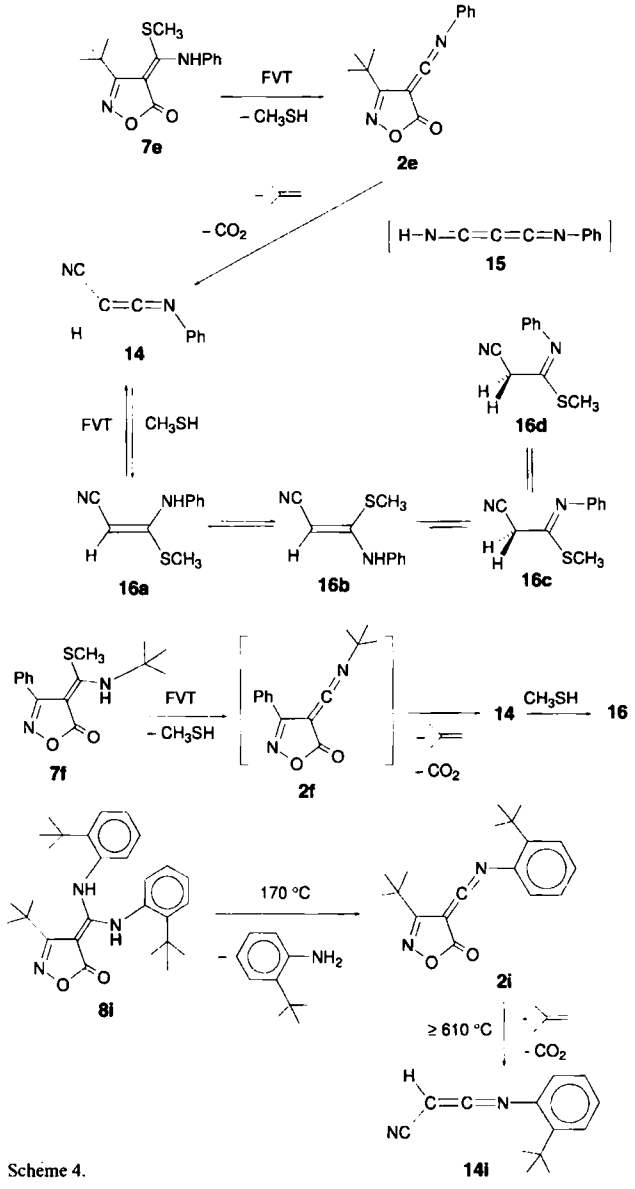
ca. −120 °C could be applied (melting point depression caused by dissolved compound). It was observed that as soon as the solvent started to melt, reaction took place. The initially slightly yellow deposits rapidly changed to a darker red and finally gave very dark solutions with a high content of possibly polymeric material. Signals for methanethiol and carbon dioxide were present in the ^{13}C NMR spectra, but no well-defined signals were attributable in the cumulene regions.[16] FVT/IR experiments, in which the products isolated as neat films at 77 K were allowed to warm up, showed that the absorptions of the bisketenimines **5** started to vanish around 170 K. This explains our difficulties in obtaining chemical and low-temperature NMR evidence for these compounds.

2. Alkyl–Aryl Substituted Isoxazolones: The 3-alkyl substituted isoxazolones are more readily sublimed than the all-aryl analogues. This means that the formation of products arising from solid-state decomposition can be almost completely suppressed.

To our initial surprise, the behavior of these compounds (Scheme 4) on FVT was quite different from the all-aryl cases **7a–d**. At 300–600 °C, **7e** eliminates methanethiol readily. In the Ar-matrix IR spectrum three very strong absorptions appear at 2091, 2071, and 1768 cm^{-1}, which we assign to the initially formed isoxazolonoketenimine **2e** (R^1 = *tert*-butyl, R^2 = phenyl) (Fig. 6a). This is in good agreement with the results obtained in the all-aryl cases (Section 1). Again, the low intensity of the CO_2 signal can be taken as evidence for an intact isoxazolone moiety.

The FVT/MS experiments demonstrate thermal loss of MeSH and formation of a species with m/z = 242 (**2e**) at 610 °C (Fig. 7b). The CAMS of this species shows loss of isobutene and CO_2 to give m/z = 142 ($\mathbf{14}^{\bullet+}$). FVT of **7e** at 750 °C generates **14** directly (m/z = 142, Fig. 7c); CAMS of $\mathbf{14}^{\bullet+}$ is dominated by m/z = 77 ($C_6H_5^+$), 114 (loss of H_2CN), 103 ($PhNC^{\bullet+}$), and 51 ($C_4H_3^+$) (Fig. 7d). Methanethiol and isobutene were themselves identified by MS/MS measurements.

With IR detection at T > 600 °C, a bisketenimine **5e** is not observed, but instead a compound with strong IR absorptions at 2050 and 2060 cm^{-1} as well as a weaker one at 2229 cm^{-1}. The signals at 2050 and 2060 cm^{-1} indicate a normal keten-



Scheme 4.

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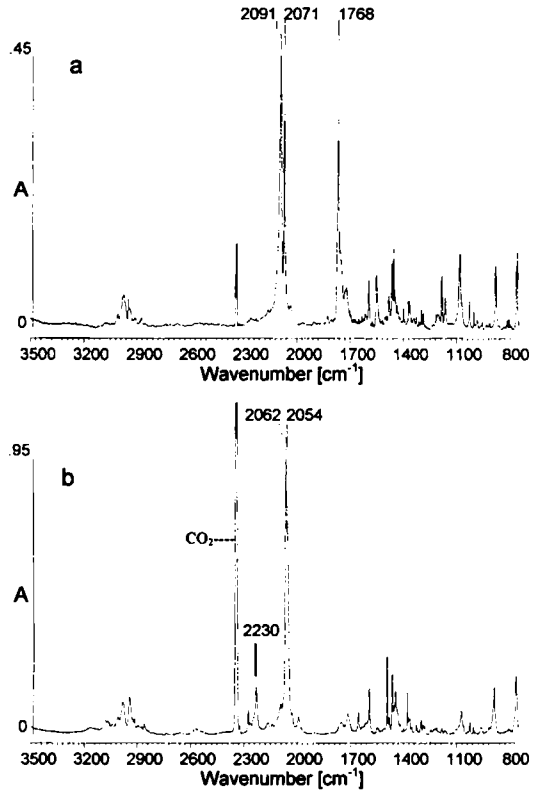


Fig. 6. IR spectra (Ar, 12 K) of the products of FVT of **7e**. a) at 610 °C (giving **2e**); b) at 770 °C (giving **14**).

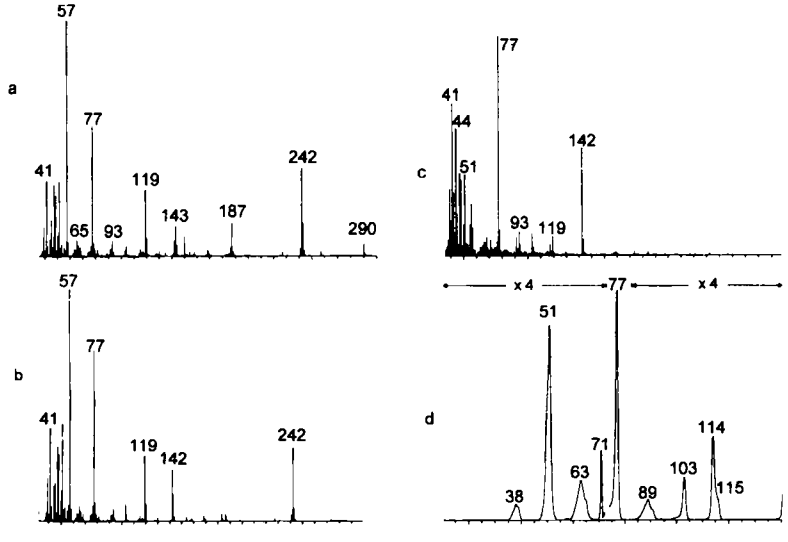


Fig. 7. a) EI-MS of **7e** at 170 °C; b) EI-MS of the product (**2e**) of FVT of **7e** at 610 °C; c) EI-MS of the product (**14**) of FVT of **7e** at 750 °C; d) CAMS of the $m/z = 142$ ion ($\mathbf{14}^{\bullet+}$) from Fig. 7c.

imine moiety, whereas the absorption at 2229 cm^{-1} strongly suggests the presence of a nitrile group. CO_2 and isobutene are also present in the matrix.[17] In agreement with the mass spectral data (vide supra), the product is identified as **14**, formed by elimination of CO_2 and expulsion of isobutene (Scheme 4).

Warming up the neat sample of **14** demonstrated that it is stable up to −90 °C; from this temperature onward its IR absorptions started to disappear. We attempted to trap the cyanoketenimine **14** with nucleophiles such as MeOH and Me_2NH. Although no products with either dimethylamino or methoxy substituents could be isolated from the product mixture, the anilino(methylthio)acrylonitrile **16** was isolated (48%) and identified by its physical and spectroscopic properties. In solution, all four possible tautomers **16** are in equilibrium[18] as determined by ^1H NMR spectroscopy. They are probably formed by trapping of cyanoketenimine **14** with MeSH—the reverse of the thermolysis reaction. It is also conceivable that the acrylonitrile **16** might be formed directly from **7e** by loss of isobutene, although intermediates were observed by IR and MS. Further, it is possible, but not likely,[19] that the monosubstituted bisiminopropadiene **15** (Scheme 4) is a precursor of **14**. No evidence for **15** was obtained by IR or MS in these FVT reactions.

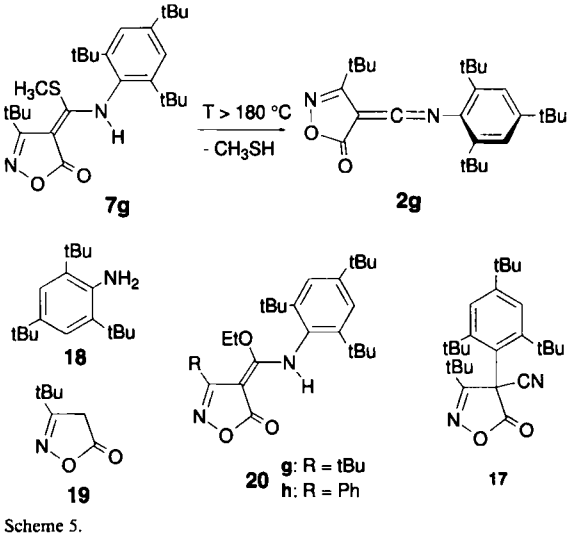
In order to clarify these issues, we subjected the acrylonitrile **16** to FVT under similar conditions. The absorptions at 2050, 2060, and 2229 cm^{-1} reappeared, indicating the formation of the cyanoketenimine **14**. Upon warming to temperatures above −80 °C these peaks started to disappear, and the absorptions of **16** reappeared. This confirms the assumption that the cyanoketenimine **14** preferably reacts with methanethiol in the course of the FVT experiments and so explains the failure to obtain other trapping products. Sulfur nucleophiles are known to be particularly reactive towards ketene-type molecules.[20] The formation of compound **14** from **16** was also unambiguously verified in an FVT/MS experiment; at temperatures above 650 °C, ions due to $\mathbf{14}^{\bullet+}$ appeared in the EIMS of **16**. The CA mass spectrum of these ions is superimposable on the spectrum shown in Fig. 7d. Thus the IR, MS and chemical evidence strongly implicates cyanoketenimine **14** as the final product.[19]

3. FVT of 7f and 8i: Similar results were obtained by inverting the substitution pattern as in **7f** (Scheme 4). Again, the formation of the cyanoketenimine **16** was observed as the final product of FVT ($\tilde{\nu} = 2060$, 2050 cm^{-1}). Interestingly, this is not only the high-temperature product, but also the only matrix-isolable product even at temperatures as low as 400 °C. The isoxazolonoketenimine **2f** was not observed. The NMR spectrum of the products formed in the melt reveals that **7f** decomposes at the melting point with evolution of methanethiol and isobutene. In the gas phase, **7f** eliminates MeSH, CO_2, and isobutene above 480 °C, as demonstrated in an FVT/MS experiment. The resulting ions at $m/z = 142$ were identical with $\mathbf{14}^{\bullet+}$ described above: the CAMS was very similar to the one shown in Fig. 7d. The other fragmentation products, MeSH, CO_2, and isobutene were identified by their CAMS also. No intermediate products were observed. The Ar-matrix IR spectrum resulting from FVT at very low temperature (300 °C) featured a weak CN band at 2240 cm^{-1}, suggesting that 4-cyano-3-phenylisoxazolone may be an intermediate.

Compound **8i** was examined by FVT/MS and IR and showed behavior very similar to that of **7e**. 2-*tert*-Butylaniline was eliminated at 170 °C, giving rise to an ion with $m/z = 298$, corresponding to **2i**. Between 610 and 750 °C, CO_2 and isobutene were eliminated with formation of a compound with $m/z = 198$, corresponding to **14i** (Scheme 4). No intermediate compounds were detected. The corresponding molecules observed by IR spectroscopy absorbed at 2101, 2083, and 1768 cm^{-1} (**2i**), and 2058 cm^{-1} (**14i**) (Ar, 12 K).

4. Isoxazolones with Sterically Demanding Substituents: The instability of the intermediates generated so far caused us to synthesize isoxazolone derivatives with bulky substituents in the hope of achieving kinetic stabilization of the products.

Unfortunately, the involatile nature of the two compounds synthesized, **7g** and **7h**, made FVT/matrix isolation experiments very difficult. We therefore decided to thermolyze the starting materials in the solid state. The normal observation upon solid-state thermolysis of isoxazolones **7a–f** was that methanethiol was formed, and the reaction mixture usually then reacted further to form numerous, probably polymeric products. In contrast, in the case of the compounds **7g** and **7h**, the evolution of MeSH was detected immediately upon reaching the melting point of the compounds. The only product of the reaction of **7g** showed a very strong IR absorption at 2231 cm^{-1} (solid), and the ^1H and ^{13}C NMR spectra suggested the formation of a 4-cyanoisoxazolone such as **17** (Scheme 5). However, this material decomposed upon heating to 200 °C in the air to form 2,4,6-tri-*tert*-butylaniline **18** and 3-*tert*-butylisoxazolone **19**. Moreover, the addition product **20g** was obtained with EtOH; this suggests that the material is a ketenimine (**2g**). The puzzling decomposition upon heating in air is unexpected for the 4-cyanoisoxazolone **17**, but may originate in the hydrolysis of **2g** to **18** and 3-*tert*-butylisoxazolone-4-carboxylic acid. The latter then decarboxylates to yield isoxazolone **19** (Scheme 5).

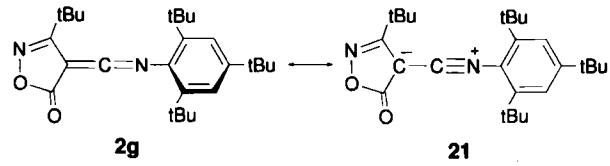


Scheme 5.

As clearly as the chemistry of this thermolysis product appears to indicate the ketenimine structure **2g**, the spectroscopic data contradict this assignment. We have shown above that typical IR absorptions for the cumulenic moiety in isoxazolonoketenimines are in the 2100 cm^{-1} region. These are themselves by no means "normal" ketenimines: the cyanoketenimines **14** have IR bands well below 2100 cm^{-1}, as is the case for most known ketenimines, which generally absorb at 2000–2050 cm^{-1}.[21] In the ^{13}C NMR spectrum, signals at $\delta = 52.2$ and 119.1 must be assigned to the ketenimine moiety; these are highly unusual values, the β- and α-carbons in ketenimines usually resonating at $\delta = 50$ and >190, respectively.[22] Such data could agree with a nitrile structure like **17**, but are incompatible with normal expectations for a ketenimine.

The matter was resolved by single-crystal X-ray crystallography. Crystals were grown within several days by slow sublimation of the crude thermolysis product of **7g** at 10^{-5} mbar and temperatures around 200 °C. The results of the structural analysis confirmed the chemical findings and also provide a rationale for the exceptional spectroscopic properties of **2g**.

Ketenimines usually possess a bent C=N–R moiety with a CNR angle close to 120° as expected for sp^2 hybridized nitrogen.[23] The C=N double bond length averages 1.27 Å in compounds with this structural entity.[23] The isomerization barrier between the two bent forms can be as high as 80 kJ mol^{-1}, and there are in fact examples of the separation of the chiral invertomers.[23, 24] The structural parameters of **2g** are totally unexpected. The C=N–R angle is 179.6(4)°, and the C=N bond length (1.151(5) Å) is almost as short as a normal CN triple bond. This indicates that the isoxazolonoketenimine **2g** is better described by the isonitrile ylide structure **21** (Scheme 6) (but still with a high degree of double bond character in the exocyclic C4–C5 bond). Selected bond lengths and angles are collected in Table 2. The ORTEP and full structural data are available.[8]



Scheme 6.

Table 2. Selected bond lengths (Å) and angles (°) in ketenimine **2g** from the X-ray crystal structure [a].

C6–N7 (C=N)	1.151(5)	C6-N7-C1	179.6(4)
C4–C6 (C=C)	1.352(5)	N7-C6-C4	173.1(4)
N1–C1′ (N–Ar)	1.412(4)	N7-C1′-C2′	117.7(4)
C1′–C2′	1.406(5)	C3-C4-C5	107.4(4)
C4–C5	1.439(6)	O1-C5-C4	104.1(5)
C3–C4	1.425(5)	O1-N2-C3	106.8(4)
N2–C3	1.298(5)	C5-O1-N2	111.1(4)
N2–O1	1.438(5)	N2-C3-C4	110.6(4)
O1–C5	1.369(5)	C4-C5-O5	133.5(5)
C5–O5	1.201(6)	O1-C5-O5	122.4(5)
C3–C22	1.504(6)	N2-C3-C22	118.8(4)

[a] The full crystallographic data are in the supplementary material of ref. [8]. The isoxazolone ring is numbered according to IUPAC conventions (O1, N2, C3, C4, C5, O5); the *tert*-butyl group at C3 is C22; the exocyclic C=N bond is C6–N7; the aryl ring is C1′, C2′, etc.

According to the structural data it is no longer a surprise that the spectroscopic properties are also not those of a "normal" ketenimine. But what is the reason for this drastic change in the structure of **2g** compared with other ketenimines? One can expect a significant electronic influence of the highly electron withdrawing isoxazolone moiety. This is documented in the relatively high values of the CCN stretch wavenumber for all the isoxazolonoketenimines. In addition to this, the extremely bulky *tert*-butyl groups in both *ortho* positions of the aromatic substituent enforce an almost linear structure, which normally is the transition state for the inversion of an sp^2 nitrogen.

Density functional calculations provide a theoretical explanation for our findings. As shown in Table 3, electron withdrawing substituents on the C-terminus lead to a decreased N-inversion barrier, higher values for the C=C=N stretching frequency, and shorter C=N bonds. This trend is in agreement with the effect already observed in the less highly substituted ketenimines **2a–f**. The theoretical (scaled) value for the C=C=N frequency in **28** (Table 3), an analogue of **2a**, is 2096 cm^{-1}, in good agreement with the experimental value for **2a** (2100 cm^{-1}). The inversion barrier in the ketenimines starts with a value higher than 50 kJ mol^{-1} in **22** and gradually decreases to approximately 9 kJ mol^{-1} in **28** (Table 3).

The frequency calculation for compound **29** (Table 3) is in extremely good agreement with experiment (calcd: 2249 cm^{-1}; expt. 2231 cm^{-1}). The predicted structure is also in excellent agreement with the X-ray crystal structure analysis, and, not

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Table 3. Calculated structural parameters [a,b], CCN stretching frequencies [a,c] (cm^{-1}), dipole moments [a] (μ, Debye), and inversion barriers [d] ($kJ\,mol^{-1}$) for substituted ketenimines ($R^1R^2C{=}C{=}NR^3$).

Species	R^1	R^2	R^3	r(C=C)	r(C=N)	∠CCN	∠CNR³	$\tilde{\nu}$(CCN)	μ	Barrier
22	H	H	H	1.313	1.230	174.4	115.4	2057 [e]	1.63	55.7
23	H	H	CH_3	1.316	1.224	176.0	122.9	2072 [f]	1.47	46.1
24	CHO	H	H	1.327	1.219	173.9	119.0	2053	3.83	37.1
25	CN	H	H	1.329	1.217	173.7	118.9	2071 [g]	4.55	38.9
26	CN	CN	H	1.344	1.207	173.2	122.5	2079 [h]	5.34	25.9
27	CN	CN	CH_3	1.351	1.196	174.3	135.0	2122 [i]	7.06	11.8
32	CN	CN	C_6H_5	1.349	1.201	174.0	137.6	2084 [j]	8.37	10.7
28	[k]	[k]	C_6H_5	1.335	1.203	174.1	137.5	2096	8.16	9.1
29	[k]	[k]	DTTP[l]	1.349	1.179	176.6	170.9[m]	2245 [n]	9.23	

[a] B3LYP/6-31G* values. [b] Bond lengths in Å and angles in degrees. [c] Scaled by a factor of 0.9613 [28]. [d] B3LYP/6-311+G**//B3LYP/6-31G* values. [e] Experimental: 2040 cm^{-1} (Ar matrix) [21a]; 2037 cm^{-1} (Ar, 12K) [35]. [f] Experimental: 2060 cm^{-1} (gas phase) [21b]. [g] CN vibration: 2255 cm^{-1}. [h] CN vibrations (asym. and sym. combinations): 2256 and 2268 cm^{-1}. [i] CN vibrations (asym. and sym. combinations): 2249 and 2264 cm^{-1}. [j] CN vibrations (asym. and sym. combinations): 2247 and 2262 cm^{-1}. Experimental value for CN and CCN stretching frequencies of **32**: 2261, 2234, and 2092 cm^{-1} (see Section 6). [k] R^1–R^2 = isoxazol-5(4*H*)-one substitutent. [l] 2,5-Di-*tert*-butylphenyl (DTTP) group. [m] The HF/6-31G* value is 178.4° [8]. [n] HF/6-31G* value, scaled by 0.8929 [34].

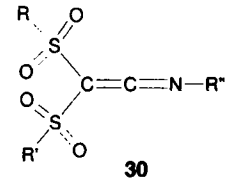
surprisingly, the (nearly) linear structure turns out to be the equilibrium structure of **29** (Table 3). The double minimum potential for the inversion of the sp^2 nitrogen becomes gradually shallower and is eventually levelled out for **29**. These compounds are no longer ketenimines in the classical sense, as they are better represented by the isonitrile ylide structure **21**. The theoretically derived dipole moments also clearly indicate that a highly polar structure is evolving with increasingly electron withdrawing C-substituents. An extremely large value of 9.23 D is predicted for **29**.

It is important to note that, while the 3-*tert*-butyl substituent in **29** is crucial for the kinetic stabilization of this compound, it is not essential for enforcing the linear ketenimine structure. The 3-phenyl derivative **2h** behaves in the same manner (IR: $\tilde{\nu}$ = 2240 cm^{-1}) although it is less stable kinetically. This product of the solid-state decomposition of **7h** at 200 °C decomposes rapidly in air. Quenching of the crude thermolysis product of **2h** with EtOH gave a product with NMR properties corresponding to compound **20h** (Scheme 5).

FVT/MS experiments corroborated the formation of **2g** and **2h**. MeSH was eliminated from **7g** already at 170 °C in the FVT/MS apparatus, giving rise to a molecule with m/z = 410, corresponding to **2g**. The molecular ion of **7g** (m/z = 458) was not observed. At 610 °C, the species with m/z = 410 disappeared owing to thermal loss of isobutene and CO_2 to give a new ion with m/z = 310 together with other species. The m/z = 310 ion corresponds to a cyanoketenimine NC–CH=C=N–$C_{18}H_{29}$ (**14g**).

Similarly, **7h** eliminated MeSH at 170 °C, giving **2h**$^{\bullet+}$ (m/z = 430). This compound did not give rise to a bisiminopropadiene (m/z = 386) at 330–610 °C, but instead decomposed to unidentified species. The ion appearing at m/z = 271 at 610 °C may be due to 2,4,6-tri-(*tert*-butyl)phenyl isocyanide or the corresponding nitrile.

Of all the ketenimines reported in the literature, there is one class, the bissulfonyl derivatives **30**, possessing spectral and X-ray structural data similar to those of **2g** and **2h**.[25] Strangely, the CNR angle decreases from 180° in **30a** (R″ = Me)[25a] to 144° in **30c** (R″ = Et);[25c] the latter value is closer to the normal angle of 120°. We have confirmed the reported[25a] linear structure of **30a** by low-temperature (−100 °C) X-ray crystallography.[26] For better comparison with **2g** and **2h**, we recorded the IR and ^{13}C NMR spectra of **30a**. The IR spectrum features

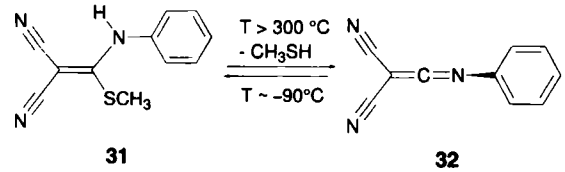


30

	R	R′	R″	∠CNC
a	CH_3	CH_3	CH_3	180°
b	CH_3	C_6H_5	CH_3	172°
c	CH_3	CH_3	C_2H_5	144°

absorptions at 2135 cm^{-1} in Ar matrix, 2170 cm^{-1} in $CHCl_3$, and 2280 cm^{-1} in the solid state. It has ^{13}C NMR signals at δ = 79 and 134 assigned to the C=C=N moiety. The NMR data are compatible with those of **2g**, but the IR spectrum in matrix and in solution is intermediate between "normal" ketenimines and the high nitrile-type value found for **2g**. The large change to 2280 cm^{-1} in the solid is unique. Perhaps complete linearity is only enforced by the crystal lattice. Further investigation of ketenimines of type **30**, particularly **30c**, is needed.[26]

6. Acrylonitriles as Precursors for Cyanoketenimines: As shown in Sections 2 and 3 (Scheme 4), cyanoketenimines **14** are the final pyrolysis products. The trapping products with methanethiol, **16**, themselves proved to be excellent precursors for cyanoketenimines. We synthesized not only **16** but also the dicyano analogue **31** by reaction of malononitrile with phenyl isothiocyanate.[27] As demonstrated by NMR and in contrast to **16**, the imine/enamine equilibrium in **31** lies exclusively on the side of the enamine form (Scheme 7). The EI mass spectra of **16** and **31** are also quite different: **16**$^{\bullet+}$ loses preferentially a MeS$^{\bullet}$ radical, whereas **31**$^{\bullet+}$ expels MeSH. FVT of **31** above 300 °C led to the expected dicyanoketenimine **32**, which shows IR absorptions at 2261 and 2234 cm^{-1} (antisymmetric and symmetric combinations of the C≡N vibrations) and 2092 cm^{-1}



31 **32**

Scheme 7.

Table 4. Calculated structural parameters [a,b] for substituted bisiminopropadienes (R^1–N=C=C*=C′=N′–R^2).

R^1	R^2	R^1–N	N–C	C–C*	C*–C′	C′–N′	N′–R^2	∠R^1NC	∠NCC*	∠CCC′	∠CC′N′	∠C′N′R^2	ϕ [c]
H	H	1.017	1.227	1.280	1.280	1.227	1.017	121.2	173.2	178.1	173.2	121.2	268.0
CH_3	H	1.448	1.217	1.285	1.278	1.230	1.017	131.9	174.8	178.4	173.0	120.3	267.8
CH_3	CH_3	1.449	1.221	1.282	1.282	1.221	1.449	130.5	174.8	179.9	174.8	130.5	267.1
CH_2=CH	H	1.320	1.225	1.279	1.281	1.227	1.017	132.6	174.4	178.3	172.9	121.5	267.7
CH_2=CH	CH_2=CH	1.391	1.224	1.280	1.280	1.224	1.391	133.2	174.3	179.3	174.3	133.2	267.1
C_6H_5	H	1.399	1.223	1.280	1.281	1.227	1.017	133.9	174.3	178.3	173.0	121.4	92.5
C_6H_5	C_6H_5	1.398	1.223	1.281	1.281	1.223	1.398	134.4	174.2	179.5	174.2	134.4	92.7

[a] B3LYP/6-31G* values. [b] Bond lengths in Å and angles in degrees. [c] ϕ = $R^1NN'R^2$ torsional angle.

(C=C=N) (Ar, 12 K) in excellent agreement with theoretical calculations ($\tilde{\nu}$/cm^{-1} (intensity/km mol^{-1}): 2262(20), 2247(40), 2084(702); B3LYP/6-31G*; cf. Table 3 and Scheme 7). Warmup experiments with **32** demonstrated that a trapping reaction with methanethiol takes place, leading to reformation of the starting material **31**. This new avenue of ketenimine chemistry is the subject of continuing investigation.[26]

7. Computational Results for Bisiminopropadienes and Their Isomers: Geometry optimizations were carried out for mono- and disubstituted bisiminopropadienes (**5**, R^1 or R^2 = H, CH_3, CH_2=CH, and C_6H_5) at the B3LYP/6-31G* level (Table 4). These compounds are characterized by rather short cumulenic C=C and C=N bond lengths (1.28 and 1.22 Å, respectively), and a slightly bent NCCCN framework. For the monosubstituted bisiminopropadienes (R^1NCCCNH), the central CCC angle is calculated to be 178°, while a 180° CCC angle is predicted for the disubstituted compounds. The isoelectronic iminopropadienones (RN=C=C=C=O) are also calculated to have a slightly bent NCCCO framework, with ∢CCC = 176–177°.[6c] All bisiminopropadienes **5** are found to have the NR^1 group almost perpendicular to the NR^2 group (ϕ = 92–93°). For comparison, the all-carbon analogue (CH_2=C=C=C=CH_2) is also calculated to have a perpendicular geometry (i.e. the methylene groups are perpendicular to each other). As seen in Table 4, the introduction of methyl, vinyl, or phenyl substituents has little effect on the optimized geometries.

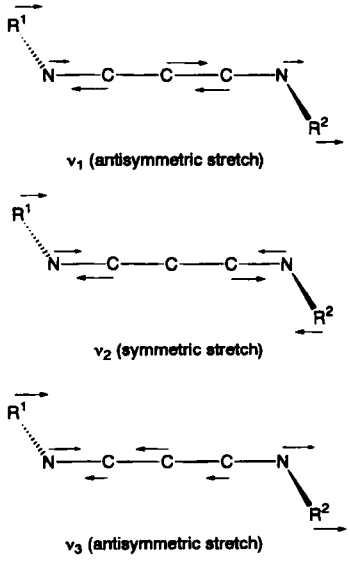
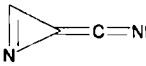


Fig. 8. Cumulenic stretching modes of R^1N=C=C=C=NR^2.

The vibrational spectra of bisiminopropadienes are characterized by three stretching vibrations ($\tilde{\nu}_1$–$\tilde{\nu}_3$, Fig. 8) of the cumulenic N=C=C=C=N skeleton: $\tilde{\nu}_1$ (2165–2210 cm^{-1}) is an antisymmetric stretching vibration with intense IR absorbance (Table 1); $\tilde{\nu}_3$ (1480–1580 cm^{-1}) is also an antisymmetric stretching vibration but with significantly lower IR intensity; and the symmetric stretching vibration ($\tilde{\nu}_2$ = 2020–2060 cm^{-1}) is infrared forbidden but Raman active. The calculated cumulenic stretching frequencies (B3LYP/6-31G*) for various substituted bisiminopropadienes and their isotopomers are given in Table 1. The standard scaling factor for B3LYP/6-31G* frequencies is 0.9613.[28] Comparison of calculated and experimental frequencies of the closely related molecules PhN=C=C=C=O and O=C=C=C=O (calcd: 2377 and 2423 cm^{-1}, respectively; expt: 2247[6c] and 2289[29] cm^{-1}, respectively) suggest that a smaller scaling factor of 0.945 is more suitable for the prediction of cumulenic stretching frequencies of bisiminopropadienes (**5**). The calculated (scaled) $\tilde{\nu}_1$ and $\tilde{\nu}_3$ frequencies for PhN=C=C=C=NPh (**5a**) (2166 and 1579 cm^{-1}, respectively) are in excellent agreement with the observed values (2167 and 1582 cm^{-1}, respectively, see Section 1). As evidenced in Table 1, the calculated isotope shifts are not sensitive to the R^1 and R^2 substituents. The magnitude of isotopomer shifts can be readily understood in terms of the involvement of the cumulated atoms in the calculated normal vibrations (Fig. 8). For **5a**, the theoretical calculations (Table 1) reproduce the experimental shifts quantitatively (Section 1).

To assess the stability of bisiminopropadienes in the gas phase, we have examined unimolecular fragmentation processes and rearrangements of the parent compound (HN=C=C=C=NH, **33**). The energy requirement (G2(MP2) level) for these reactions are summarized in Table 5. The energetically most favorable fragmentation reaction of **33** is the loss of a hydrogen atom, calculated to be endothermic by 319 kJ mol^{-1}. Dissociation of **33** to HNC + CCNH is also predicted to be highly endothermic (375 kJ mol^{-1}). Note that the products of this fragmentation can rearrange to more stable isomers, namely, HCN and HCCN. However, this "nonlinear" dissociation is still calculated to be endothermic (by 217 kJ mol^{-1}). Cyanoketenimine (**34**) is 99 kJ mol^{-1} more stable than bisiminopropadiene. However, the rearrangement of **33** to **34** through a 1,3-hydrogen shift (TS **39**) has a high activation barrier of 383 kJ mol^{-1}. Amino(cyano)acetylene (H_2N–C≡C–CN, **35**) is calculated to lie 50 kJ mol^{-1} below **33**. The transition structure (**40**) for the rearrangement of **33** to **35** lies 273 kJ mol^{-1} above **33**. Hence, **33** is predicted to be a stable and observable species in the gas phase, in accord with the mass spectrometric NRMS results.[7b] However, it should be noted that the unsubstituted molecules **33**, **34**, and **35** are all expected to tautomerize rapidly to malononitrile (NC–CH_2–CN, **36**) activated by wall collisions in FVT experiments.[4b, 7b–c] Finally, we note that azirineketenimine (**37**) is calculated to be a formally stable species on the $C_3H_2N_2$ potential energy surface, albeit 150 kJ mol^{-1} less stable than bisiminopropadiene (**33**). The triplet nitrene :Ṅ–CH=C=C=NH (**38T**) is a high energy isomer, lying 209 kJ mol^{-1} above bisiminopropadiene (**33**). The singlet nitrene :Ṅ–CH=C=C=NH is predicted not to be a stable equilibrium structure, collapsing without going through a barrier to azirineketenimine (**37**).

Table 5. Calculated total energies (hartrees) and relative energies (kJ mol^{-1}) of HNCCCNH, HNCCCNH$^{\cdot+}$, and related species [a,b].

Molecules	Total E	Relative E
HN=C=C=C=NH (**33**)	−224.55096	0.0
NC–CH=C=NH (**34**)	−224.58880	−99.3
H_2N–C≡C–CN (**35**)	−224.57030	−50.8
NC–CH_2–CN (**36**)	−224.61787	−175.7
 (**37**)	−224.49375	150.2
:Ṅ–CH=C=C=NH (**38T**)	−224.47135	209.0
TS(**33** → **34**) (**39**)	−224.40501	383.2
TS(**33** → **35**) (**40**)	−224.44711	272.7
HCCN + HCN	−224.46849	216.5
HNCCCN$^{\cdot}$ + H$^{\cdot}$	−224.42949	318.9
HNCC + CNH	−224.40805	375.3
HNCCC + NH	−224.29351	675.9
HNCCCNH$^{\cdot+}$ (**33**$^{\cdot+}$)	−224.22919	0.0
HNCC$^{\cdot+}$ + CNH	−224.05437	459.0
HNCCCN^{+} + H$^{\cdot}$	−224.06293	436.5
HNCC + CNH$^{\cdot+}$	−223.96316	698.5
HNCCCN$^{\cdot}$ + H^{+}	−223.92949	786.9
HNCCC$^{\cdot+}$ + NH	−223.92870	788.9
HNCCC + NH$^{\cdot+}$	−223.86627	952.9

[a] G2(MP2) E_0 values. [b] Calculated G2(MP2) E_0 values include −223.92949 (HNCCCN$^{\cdot}$), −223.56293 (HNCCCN^{+}), −169.21800 (HNCCC), −168.85318 (HNCCC$^{\cdot+}$), −131.14755 (HNCC), −130.79390 (HNCC$^{\cdot+}$), −131.18607 (HCCN), −93.26048 (HNC), −92.81561 (HNC$^{\cdot+}$), −93.28243 (HCN), −55.07552 (NH), and −54.64827 (NH$^{\cdot+}$).

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The radical cation of **33** is predicted to have a strongly bent structure, with ∢CCC = 128°. The calculated fragmentation energies of $33^{\cdot+}$ are given in Table 5. The most favorable fragmentation reactions of $33^{\cdot+}$ correspond to the loss of a hydrogen atom and the loss of HNC. All other fragmentation processes are considerably higher in energy (> 700 kJ mol^{-1}). These results are in good accord with mass spectral results for **5a** reported in Section 1 (Fig. 2b). The (adiabatic) ionization energy of **33** is predicted to be 8.76 eV at the G2(MP2) level of theory.

Conclusions

FVT of isoxazolones **7–9** results in the formation of isoxazolonoketenimines **2**, usually as transient intermediates, detectable by Ar-matrix IR spectroscopy. Loss of CO_2 with rearrangement leads to bisiminopropadienes **5**, especially when the migrating group R^1 is aryl. The compounds **5** are isolable in Ar matrices at cryogenic temperatures, or as neat solids at 77 K, but undergo reaction (polymerization) as soon as the solvent thaws or diffusion becomes important in the solid (ca. −100 °C).

Ketenimines **2g** and **2h** have highly unusual linear C=C=N–C frameworks, as revealed in the X-ray structure of **2g** and the exceptional ^{13}C NMR and IR spectroscopic data. These compounds are best described as resonance hybrids of ketenimines and isonitrile ylides, $R_2\bar{C}-\overset{+}{C}\equiv N-R'$. Methylthio-substituted enamines **16** and **31** were found to be convenient precursors of *C*-cyanoketenimines **14** and **32**.

Experimental and Computational Procedure

Computational Method: Ab initio [30] and density functional calculations were carried out with the GAUSSIAN 92/DFT series of programs [31]. The structures of bisiminopropadienones ($R^1N=C=C=C=NR^2$) and ketenimines ($R^1R^2C=C=NR^3$) were optimized with the 6-31 G* basis set [30] using the B3LYP formulation [32] of density functional theory, i.e., Becke's three-parameter exchange functional [32a] and Lee–Yang–Parr correlation functional [32b]. Harmonic vibrational frequencies and infrared intensities were predicted at this level by using analytical second derivatives. The directly calculated B3LYP/6-31 G* frequencies were scaled by a factor of 0.9613 to account for their average overestimation at this level of theory [28]. The energies of the neutral and the radical cation of HN=C=C=C=NH were investigated by the Gaussian-2 [G2(MP2)] theory. The G2(MP2) method, described in detail elsewhere [33], is a composite procedure based effectively on QCISD(T)/6-311 + G(3df,2p)//MP2/6-31 G* energies (evaluated by making certain additivity assumptions) together with zero-point vibrational and isogyric corrections. Spin-restricted calculations were used for closed-shell systems and spin-unrestricted for open-shell systems. The frozen-core approximation was employed for all correlation calculations.

General Experimental Methods: The general procedure and apparatus for FVT experiments have been described in detail elsewhere [36]. Here we will only give a brief overview of the methods employed. In the analytical matrix isolation experiments, the quartz thermolysis tube (10 cm × 0.8 cm i.d.) was directly attached to the cold head of a closed cycle liq. He cryostat. Codeposition of the FVT products with a carrier gas (Ar) took place on an IR window (BaF_2), which was cooled to ca. 12–22 K. After deposition, the cold head was placed in the optical pathway of an FTIR spectrometer (Perkin-Elmer 1720X; resolution 0.5 cm^{-1}) for spectral analysis.

For the determination of thermal stabilities and intermolecular interactions it is often useful to deposit reactive species without a matrix host. For this purpose, the products were deposited neat onto a spectroscopic window at 12 K or 77 K (liq. N_2). The materials could subsequently be warmed progressively to room temperature. An analogous apparatus allowing product and solvent deposition on a cold finger at 77 K and subsequent thawing permited the isolation of products in low temperature solutions for NMR spectroscopy.

FVT/MS experiments were performed on a six-sector VG AutoSpec 6 F spectrometer (E_1, B_1, E_2, E_3, B_2, E_4 geometry; E = electric, B = magnetic sector) with the quartz thermolysis tube installed directly in the source housing [37]. In the CA experiments, a beam of ions was mass-selected with a combination of three sectors and submitted to collisional activation with oxygen (60–80% transmittance). The fragments were recorded by scanning the field of the third electric sector and collecting the ions in the fifth field-free region with an off-axis photomultiplier dectector. In some experiments (e.g., Fig. 4), the fragments were recorded by linked scanning of the fields of the last three sectors and collecting the ions just after the last electric sector (E_4). Typical conditions were 8 kV accelerating voltage, 200 A trap current, and 200 °C source temperature. Electron ionization (EI) MS used 70 eV ionizing energy. The samples were introduced into the source or into the thermolysis tube with a conventional direct insertion probe.

Materials: ^{13}C-Carbon disulfide (99 atom% ^{13}C) and ^{15}N-aniline (99 atom% ^{15}N) were obtained from Cambridge Isotope Laboratories, Woburn, MA, USA. 3-Substituted isoxazolone-5(4*H*)-ones were prepared according to the literature [12] and converted to the 4-bis(methylthio)methylene derivatives **6** by the previously published method for **6j** [4b]. Data are given below.

4-[(Bismethylthio)methylene]-3-phenylisoxazol-5(4*H*)-one (6a): Yield: 83%. Yellow crystals, m.p. 142–143 °C; IR (CCl_4): $\tilde{\nu}$ = 2927 (m), 1732 (s), 1503 (s), 1367 (m), 1260 (s), 1119 (m), 1076 (m), 1009 (m) cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.15 (s, 3H, CH_3), 2.76 (s, 3H, CH_3), 7.6–7.4 (m, 5H, arom.); ^{13}C NMR ($CDCl_3$): δ = 20.5 (CH_3), 22.4 (CH_3), 106.4 (C-4), 128.0, 128.5, 129.1, 130.3 (arom.), 161.1 (C-3), 167.0 (=$C(S)_2$), 185.4 (C-5); MS: *m/z* = 265 (M^+, 71%), 150 (77), 149 (74), 145 (39), 103 (20), 100 (29), 77 (37), 75 (79), 57 (33), 44 (100). HRMS: calcd for $C_{12}H_{11}O_2NS_2$: 265.0231; found 265.0230.

4-[(Bismethylthio)methylene]-3-*p*-tolylisoxazol-5(4*H*)-one (6c): Yield: 61%. Yellow crystals, m.p. 138 °C; IR (KBr): $\tilde{\nu}$ = 1734, 1718 cm^{-1} (CO); ^1H NMR (200 MHz, $CDCl_3$): δ = 2.18 (s, 3H, CH_3), 2.42 (s, 3H, SCH_3), 2.80 (s, 3H, SCH_3), 7.25 (d, *J* = 7.8 Hz, 2H, aromatic), 7.44 (d, *J* = 7.8 Hz, 2H, aromatic); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.8, 21.5, 22.5, 106.5, 126.2, 127.9, 129.4, 140.7, 161.1, 167.2, 185.3; UV: λ_{max} = 207, 228, 319, 388 nm; $C_{13}H_{13}NO_2S_2$ (279.4): Anal. calcd C 55.9 H, 4.69, N 5.01; found: C 55.6, H 4.68, N 4.91.

4-[(Bismethylthio)methylene]-3-*tert*-butylisoxazol-5(4*H*)-one (6e): Yield: 63%. Orange crystals, m.p. 104 °C; IR (KBr): $\tilde{\nu}$ = 1713 cm^{-1} (CO); ^1H NMR (200 MHz, $CDCl_3$): δ = 1.45 (s, 9H, *t*Bu), 2.73 (s, 3H, SCH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.5, 29.3, 34.8, 108.2, 167.3, 168.1, 183.8; UV: λ_{max} = 301, 417 nm; $C_{10}H_{15}NO_2S$: calcd 245.0544; found 245.0532 (HRMS). Anal. calcd C 48.95, H 6.16, N 5.71; found: C 48.51, H 6.58, N 5.94.

Standard Procedure for Synthesis of Isoxazolones 7: The amine (1 mmol) was added to **6** (1 mmol) dissolved in THF (10–15 mL). The rection mixture was stirred at RT and monitored by TLC. When no more changes could be detected by TLC (usually 20–24 h) the solvent was evaporated in vacuo and the crude product either recrystallized (usually THF/pentanes) or subjected to column chromatography (SiO_2, methylene chloride/methanol). Data are given below.

Standard Procedure for Synthesis of Isoxazolones 8: Either **6** or **7** (1 mmol) was dissolved in THF and an excess (at least twofold) of the amine was added. The mixture was stirred at RT or under reflux and monitored by TLC. The product usually precipitated, and was filtered and washed with THF. Data are given below.

Standard Procedure for Synthesis of Isoxazolones 9: A solution of **7** (2.0 mmol) and dimethylamine (2.0 mmol as a 30% aqueous solution) in THF (20 mL) was refluxed for 48 h. The precipitate formed was chromatographed on SiO_2. The product eluted with methylene chloride/methanol (10:1 to 30:1 v/v). Data are given below.

3-Phenylisoxazolones:

4-[(*N*-Phenylamino)(methylthio)methylene]-3-phenylisoxazol-5(4*H*)-one (7a): Pale yellow crystals, 91%; m.p. 162 °C; IR (KBr): $\tilde{\nu}$ = 1686 cm^{-1} (CO); ^1H NMR (200 MHz, $CDCl_3$): δ = 1.81 (s, 3H, SCH_3), 7.33–7.60 (m, 10H, arom.); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 17.6, 92.7, 124.8, 127.7, 128.2, 128.9, 129.6, 129.8, 130.4, 137.3, 161.9, 167.9, 173.9; UV: λ_{max} = 207, 267, 359 nm; $C_{17}H_{14}N_2O_2S$: calcd 310.0776; found 310.0775 (HRMS). Anal. calcd C 65.79, H 4.55, N 9.03; found: C 66.01, H 4.61, N 8.92.

4-[(*N*-Phenylamino)(methylthio)methylene]-3-phenylisoxazol-5(4*H*)-one (11): Pale yellow crystals prepared in the same manner as **7a** with ^{15}N-aniline in 69% yield, m.p. 142 °C; IR (KBr): $\tilde{\nu}$ = 1687 cm^{-1} (CO); ^1H NMR (200 MHz, $CDCl_3$): δ = 1.81 (s, 3H, SCH_3), 7.29–7.59 (m, 10H, arom.); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 17.5, 92.6, 124.7 (d, *J* = 1.5 Hz), 127.7, 128.2, 128.9, 129.6 (d, *J* = 1.5 Hz), 129.8, 130.4, 137.2, 161.9, 167.9 (d, *J* = 1.5 Hz), 173.8.

4-[(*N*-Phenylamino)(methylthio)-^{13}C-methylene]-3-phenylisoxazol-5(4*H*)-one (13): Prepared from $^{13}CS_2$ via **6a** in the same manner as described for **7a**. Yellow crystals, 87%; IR (KBr): $\tilde{\nu}$ = 1681 cm^{-1} (CO); ^1H NMR (200 MHz, $CDCl_3$): δ = 1.81 (d, $^3J_{H,C}$ = 4.4 Hz, 3H, SCH_3), 7.25–7.55 (m, 10H, arom.); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 17.6, 93.6, 124.8, 127.8, 128.3, 129.0, 129.7, 129.9, 130.5, 137.3, 161.9, 167.8 (vs), 173.6.

4-[(*N*-p-Tolylamino)(methylthio)methylene]-3-phenylisoxazol-5(4*H*)-one (7b): Pale yellow crystals, 95%, m.p. 167 °C; IR (KBr): $\tilde{\nu}$ = 1686 cm^{-1} (CO); ^1H NMR

(200 MHz, $CDCl_3$): $\delta = 1.80$ (s, 3H, SCH_3), 2.37 (s, 3H, CH_3), 7.23 (s, 5H, arom.), 7.38–7.62 (m, 4H, arom. H); ^{13}C NMR: δ = (50 MHz, $CDCl_3$) 17.6, 21.1, 92.2, 124.7, 128.2, 128.9, 129.8, 130.5, 130.6, 134.6, 138.0, 161.9, 167.9, 174.1; $C_{18}H_{16}N_2O_2S$: calcd 324.0925; found 324.0932 (HRMS). Anal. calcd C 66.64, H 4.97, N 8.63; found: C 66.79, H 5.05, N 8.52.

4-[(*N*-*tert*-Butylamino)(methylthio)methylene]-3-phenylisoxazol-5(4*H*)-one (7f): Pale yellow crystals, 70%, m.p. 162 °C; IR (KBr): $\tilde{\nu} = 1682\ cm^{-1}$ (CO), ^1H NMR (200 MHz, $CDCl_3$): $\delta = 1.57$ (s, 9H, *t*Bu), 1.94 (s, 3H, SCH_3), 7.4–7.7 (m, 5H, arom.), 9.98 (br s, 1H, NH); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 19.3, 29.8, 56.9, 88.5, 128.2, 128.5, 129.8, 130.2, 161.3, 170.7, 174.4$; UV: $\lambda_{max} = 266, 361$ nm; $C_{15}H_{18}N_2O_2S$: calcd 290.1089; found 290.1090 (HRMS). Anal. calcd C 62.04, H 6.25, N 9.64; found C 61.86, H 6.33;, N 9.68.

4-[(*N*-Methylamino)(methylthio)methylene]-3-phenylisoxazol-5(4*H*)-one (7m): Yellow solid, 75%, m.p. 168 °C; IR (KBr): $\tilde{\nu} = 1682\ cm^{-1}$ (CO); ^1H NMR (200 MHz, $CDCl_3$): $\delta = 1.96$ (s, 3H, SCH_3), 3.31 (d, $J = 5.1$ Hz, 3H, NCH_3), 7.42–7.63 (m, 5H, arom.), 8.95 (q, $J = 5.1$ Hz, 1H, NH); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 18.2, 32.7, 88.9, 128.1, 128.6, 129.8, 130.4, 161.4, 171.7, 174.7$; $C_{12}H_{12}N_2O_2S$: calcd 248.0630; found 248.0625 (HRMS).

4-[Bis(*N*-*p*-tolylamino)methylene]-3-phenylisoxazol-5(4*H*)-one (8b): ^1H NMR (200 MHz, $CDCl_3$): $\delta = 2.08$ (s, 6H, CH_3), 6.58 (br s, 2H, NH), 6.68–7.51 (m, 13H, arom.); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 20.9, 79.3, 120.0, 123.9, 126.8, 128.2, 128.5, 129.1, 130.1, 130.3, 135.5, 138.8, 153.6, 160.5, 176.2$.

4-[(*N*,*N*-Dimethylamino)(*N*-phenylamino)methylene]-3-phenylisoxazol-5(4*H*)-one (9a): Pale yellow crystals, 45%; m.p. 162 °C; IR (KBr): 1654 cm^{-1} (CO); ^1H NMR (200 MHz, [D$_6$]DMSO): $\delta = 3.18$ (s, 6H, NCH_3), 6.47–6.51 (m, 2H, arom.), 6.90–7.27 (m, 8H, arom. H), 9.21 (br s, 1H, NH); ^{13}C NMR (50 MHz, [D$_6$]DMSO): $\delta = 41.0, 77.0, 121.7, 124.3, 126.9, 128.2, 128.6, 129.0, 130.3, 138.6, 158.9, 163.1, 174.5$; $C_{18}H_{17}N_3O_2$: calcd 307.1321; found 307.1317 (HRMS). Anal. calcd C 70.34, H 5.57, N 13.67, found C 70.48, H 5.58, N 13.13.

4-[(*N*,*N*-Dimethylamino)(*N*-*p*-*tolylamino*)methylene]-3-phenylisoxazol-5(4*H*)-one (9b): Colorless needles, 56%, m.p. 140 °C; IR (KBr): $\tilde{\nu} = 1664\ cm^{-1}$ (CO); ^1H NMR (200 MHz, [D$_6$]DMSO): $\delta = 2.19$ (s, 3H, CH_3), 3.06, 3.17 (s, 3H, NCH_3), 6.35 (d, $J = 8.0$ Hz, 2H), 6.72 (d, $J = 8.0$ Hz, 2H), 6.99–7.30 (m, 5H, arom.), 9.22 (br s, 1H, NH); ^{13}C NMR (50 MHz, [D$_6$]DMSO): $\delta = 20.6, 40.7, 77.0, 121.7, 126.7, 128.1, 129.0, 130.1, 134.0, 135.7, 158.8, 163.0, 174.6$; $C_{19}H_{19}N_3O_2$: calcd 321.1476; found 321.1481 (HRMS).

3-*p*-Tolylisoxazolones:

4-[(*N*-phenylamino)(methylthio)methylene]-3-*p*-tolylisoxazol-5(4*H*)-one (7c): Pale yellow crystals, 65%, m.p. 162 °C; IR (KBr): $\tilde{\nu} = 1685\ cm^{-1}$ (CO); ^1H NMR (200 MHz, $CDCl_3$): $\delta = 1.82$ (s, 3H, SCH_3), 2.41 (s, 3H, CH_3), 7.22–7.47 (m, 9H, arom.); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 17.6, 21.4, 92.7, 124.8, 127.5, 127.7, 128.8, 128.9, 129.6, 137.3, 139.9, 161.9, 167.9, 174.0$; UV: $\lambda_{max} = 206, 227, 310, 358$ nm; $C_{18}H_{16}N_2O_2S$ (324.4): Anal. calcd C 66.6, H 4.97, N 8.64; found: C 66.2, H 5.04, N 8.34.

4-[(N-p-tolylamino)(methylthio)methylene]-3-*p*-tolylisoxazol-5(4*H*)-one (7d): Pale yellow crystals, 43%, m.p. 185 °C; IR (KBr): $\tilde{\nu} = 1686\ cm^{-1}$ (CO); ^1H NMR (200 MHz, $CDCl_3$): $\delta = 1.81$ (s, 3H, SCH_3) 2.37, 2.41 (s, 3H, CH_3), 7.34 (dd, 4H, arom.), 11.73 (br s, 1H, NH); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 17.6, 21.0, 21.4, 92.2, 124.7, 127.5, 128.7, 128.9, 130.1, 134.6, 137.9, 139.9, 162, 168.1, 174.0$; UV: $\lambda_{max} = 286, 368$ nm; HRMS $m/z = 338.1091$ (calcd for $C_{19}H_{18}N_2O_2S$, 338.1089); $C_{19}H_{18}N_2O_2S$ (338.4): Anal. calcd C 67.43, H 5.36, N 8.28; found C 67.33, H 5.36, N 8.35.

4-[(*N*,*N*-Dimethylamino)(*N*-phenylamino)methylene]-3-*p*-tolylisoxazol-5(4*H*)-one (9c): Colorless crystals, 25%, m.p. 102 °C; IR (KBr): $\tilde{\nu} = 1638\ cm^{-1}$ (CO); ^1H NMR (200 MHz, [D$_6$]DMSO): $\delta = 2.30$ (s, 3H, CH_3), 3.06 (s, 6H, NCH_3), 6.98–7.01 (m, 9H, arom.); ^{13}C NMR (50 MHz, [D$_6$]DMSO): $\delta = 21.3, 41.1, 77.7, 121.6, 124.6, 126.8, 127.7, 128.8, 129.0, 138.7, 139.2, 159.0, 162.8, 174.5$; UV: $\lambda_{max} = 206, 227, 259$ nm; $C_{19}H_{19}N_3O_2$: calcd 321.1477; found 321.1476 (HRMS).

3-*tert*-Butylisoxazolones:

4-[(*N*-Phenylamino)(methylthio)methylene]-3-*tert*-butylisoxazol-5(4*H*)-one (7e): Pale yellow crystals, 70%, m.p. 133 °C; IR (KBr): $\tilde{\nu} = 1664$ (CO) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 1.33$ (s, 9H, *t*Bu), 1.85 (s, 3H, SCH_3), 7.08–7.25 (m, 5H, arom.), 12.33 (br s, 1H, NH); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 17.3, 29.0, 34.5, 94.6, 124.5, 127.3, 129.7, 138.5, 164.8, 167.7, 175.4$; UV: $\lambda_{max} = 275, 385$ nm; $C_{15}H_{18}N_2O_2S$: calcd 290.1089; found 290.1088 (HRMS). Anal. calcd C 62.04, H 6.25, N 9.64; found: C 61.99, H 6.57, N 9.54.

4-[(*N*-(2,4,6-tri-*tert*-butylphenylamino)(methylthio)methylene]-3-*tert*-butylisoxazol-5(4*H*)-one (7g): This compound was not obtainable by the standard procedure. Butyllithium (2.05 mmol as a 2.4 M hexane solution) was added to a solution of 2,4,6-tri-*tert*-butylaniline (535 mg, 2.05 mmol) in dry THF (15 mL) at RT. The mixture was stirred for 30 min at RT and **6e** (0.50 g, 2.05 mmol) in THF (10 mL) was added. The resulting mixture was stirred at RT for 36 h and concentrated to a small volume. Column chromatography on SiO_2, with methylene chloride/pentane 1:1 as eluent, resulted in a 60% recovery of 2,4,6-tri-*tert*-butylaniline, as well as 313 mg (32%) of **7g**, which was slightly less polar than **6e** and absorbs strongly at 254 nm (TLC). Recrystallization from THF/pentane afforded colorless crystals, m.p. 180 °C; IR (KBr): $\tilde{\nu} = 1664\ cm^{-1}$ (CO); ^1H NMR (200 MHz, $CDCl_3$): $\delta = 1.33$ (s, 9H, *t*Bu), 1.41 (s, 18H, *t*Bu), 1.50 (s, 9H, *t*Bu), 1.57 (s, 3H, SCH_3), 7.40 (s, 2H, arom.); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 16.0, 29.1, 31.4, 32.0, 34.3, 35.0, 36.8, 89.1, 123.3, 130.4, 148.2, 151.4, 167.4, 167.6, 176.5$; UV: $\lambda_{max} = 269, 360$ nm; $C_{27}H_{42}N_2O_2S$: calcd 458.2967; found 458.2959 (HRMS). Anal. calcd C 70.70, H 9.23, N, 6.11; found C 70.60, H 9.66, N 5.79.

4-[(Ethoxy)(*N*-2,4,6-tri-*tert*-butylphenylamino)methylene]-3-*tert*-butylisoxazol-5-(4*H*)-one (20g): Ketenimine **2g** (20 mg, 0.05 mmol) was refluxed with abs. EtOH (5 mL) for 10 min. After removal of excess solvent, a colorless solid remained (20 mg, 91%), m.p. 181 °C; IR (KBr): $\tilde{\nu} = 1664\ cm^{-1}$ (CO); ^1H NMR (200 MHz, $CDCl_3$): $\delta = 1.13$ (t, 3H, OCH_2CH_3), 1.33 (s, 9H, *t*Bu), 1.34 (s, 9H, *t*Bu), 1.40 (s, 18H, *t*Bu), 3.60 (q, 2H, OCH_2CH_3), 7.41 (s, 2H, arom. H), 12.63 (br s, 1H, NH); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 15.1, 28.0, 31.3, 31.5, 34.1, 35.1, 36.3, 69.2, 79.5, 122.9, 129.3, 147.7, 151.6, 163.0, 168.2, 178.4$; UV: $\lambda_{max} = 295$ nm; $C_{28}H_{44}N_2O_3$: calcd 456.3351; found 456.3353 (HRMS). Anal. calcd C 73.64, H 9.71, N 6.13; found C 73.28, H 9.53, N 6.03.

***tert*-Butylketenimine 2g**: Isoxazolone **7g** (45 mg, 0.1 mmol) was heated to the melting point (180 °C) in a glass tube under N_2 until gas evolution ceased. The crude product was purified by sublimation (10^{-5} mbar, 200 °C). Yield: 34 mg (83%) **2g**, pale yellow crystals; m.p. 220 °C; IR (Ar matrix, 12 K): $\tilde{\nu} = 2226, 2223$ (CCN), 1740 (CO); IR (KBr): $\tilde{\nu} = 2231, 1720$; IR ($CHCl_3$): $\tilde{\nu} = 2229, 1720, 1705$; IR ($CCl_4$): $\tilde{\nu} = 2221, 1724\ cm^{-1}$; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 1.34$ (s, 9H, *t*Bu), 1.35 (s, 9H, *t*Bu), 1.48 (s, 18H, *t*Bu), 7.48 (s, 2H, arom.); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 28.7, 30.3, 31.1, 34.1, 35.8, 35.9, 52.3, 119.9, 122.9, 131.3, 150.7, 155.7, 169.4, 176.4$; $C_{26}H_{38}N_2O_2$: calcd 410.2933; found 410.2935 (HRMS); X-ray structure: ref. [8].

4-[(*N*-(2,4,6-tri-*tert*-butylphenylamino)(methylthio)methylene]-3-phenylisoxazol-5-(4*H*)-one (7h) was prepared in the same manner as described for **7g**. The product from chromatography (250 mg) was purified by sublimation at 70 °C for 16 h. Yield: 7%, colorless crystals, m.p. 197 °C; IR (KBr): $\tilde{\nu} = 1682\ cm^{-1}$ (CO); ^1H NMR (200 MHz, $CDCl_3$): $\delta = 1.30$ (s, 9H, *t*Bu), 1.39 (s, 18H, *t*Bu), 1.49 (s, 3H, SCH_3), 7.4–7.6 (m, 7H, arom.), 12.2 (br s, 1H, NH); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 17.5, 31.3, 32.1, 35.0, 36.5, 123.3, 128.3, 128.5, 129.8, 130.6, 130.7, 147.4, 151.2, 161.3, 173.4, 175.3$; UV: $\lambda_{max} = 266, 357$ nm; $C_{29}H_{38}N_2O_2S$: calcd 478.2654; found 478.2649 (HRMS). Anal. calcd C 72.76, H 8.00, N 5.85; found: C 72.58, H 8.03, N 5.74.

Ketenimine 2h: Methylthioisoxazolone **7h** (ca. 200 mg) was heated to its melting point. The compound started decomposing, seen by gas evolution and change of color from light yellow to dark brown and later black. The crude product was subjected to IR and NMR investigations and showed signals that could be assigned to a mixture of starting material **7h** and ketenimine **2h**, by comparison with the data obtained for the *tert*-butylketenimine **2g**. IR (KBr): $\tilde{\nu} = 2240\ cm^{-1}$ (CCN); ^1H NMR (200 MHz, $CDCl_3$): $\delta = 1.33$ (s, *t*Bu), 1.35 (s, *t*Bu), 7.36–7.68 (m, arom.); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 29.9, 31.0, 35.7, 35.7, 54.3, 119.5, 122.8, 126.4, 128.0, 128.9, 130.3, 130.7, 150.4, 155.8, 160.3, 167.1, 175.3$.

4-[(Ethoxy)(*N*-2,4,6-tri-*tert*-butylphenylamino)methylene]-3-phenylisoxazol-5(4H)-one (20h): The crude thermolysis product from **7h** containing ketenimine **2h** and isoxazolone **7h** was refluxed with EtOH for 10 min. The remaining mixture was investigated by NMR and showed the signals of isoxazolone **7h** and the trapping product **20h**. ^1H NMR (200 MHz, $CDCl_3$): $\delta = 0.60$, (t, OCH_2), 1.33 (s, *t*Bu), 1.42 (s, *t*Bu), 3.34 (q, CH_3), 7.36–7.61 (m, arom.), 11.6 (br s, NH); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 14.3, 31.2, 31.6, 34.8, 36.2, 69.7, 80.1, 122.9, 127.9, 127.9, 128.4, 129.4, 130.3, 147.4, 151.3, 164.8, 177.1, 185.8$.

4-[Bis(*N*-*o*-*tert*-butylamino)methylene]-3-*tert*-butylisoxazol-5(4*H*)-one (9i): Yield: 39% based on the amine after 48 h of reflux in THF; m.p. 190 °C (decomp); IR (KBr): $\tilde{\nu} = 1650$ (s), 1514 (m), 1479 (m), 1444 (m), 758 (m) cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.41$ (s, 9H, *t*Bu), 1.44 (s, 9H, *t*Bu), 6.75–7.31 (m, 8H, arom.), 9.2 (br s, 2H, NH); ^{13}C NMR ($CDCl_2$): $\delta = 29.5$ (q), 31.0 (q), 33.8 (s), 35.2 (s), 80.9 (s), 125.4 (d), 126.3 (d), 126.8 (d), 127.5 (d), 134.3 (s), 141.3 (s), 154.5 (s), 166.8 (s), 177.3 (s); MS: $m/z = 447$ (M^+), 403, 388, 149, 57; $C_{28}H_{37}N_3O_2$: calcd 447.2886, found 447.2892 (HRMS). Anal. calcd C 75.1, H 8.3, N 9.4; found C 74.8, H 8.5, N 8.7.

3-Methylisoxazolones:

4-[(*N*-Phenylamino)(methylthio)methylene]-3-methylisoxazol-5(4*H*)-one (7j): Pale yellow crystals, 97%, m.p. 141 °C; IR (KBr): $\tilde{\nu} = 1687\ cm^{-1}$ (CO); ^1H NMR (200 MHz, $CDCl_3$): $\delta = 1.99$ (s, 3H, SCH_3), 2.40 (s, 3H, CH_3), 7.39–7.43 (m, 5H, arom.); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 15.8, 16.7, 94.6, 124.5, 127.5, 129.8, 137.5, 158.8, 165.4, 173.7$; UV: $\lambda_{max} = 356$ nm; $C_{12}H_{12}N_2O_2S$ (216.3): Anal. calcd C 58.0, H 4.87, N 11.2; found: C 57.8, H, 4.86, N 11.1.

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4-[(*N*-*p*-Tolylamino)(methylthio)methylene]-3-methylisoxazol-5(4*H*)-one (7k): Pale yellow crystals, 85%, m.p. 154 °C; IR (KBr): $\tilde{\nu}$ = 1696 cm^{-1} (CO); ^1H NMR (200 MHz, $CDCl_3$): δ = 2.02 (s, 3H, SCH_3), 2.39 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 7.25–7.27 (m, 4H, arom.); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.9, 16.7, 21.1, 94.4, 124.5, 130.4, 134.9, 137.7, 158.8, 165.4, 173.9; UV: λ_{max} = 204, 228, 345 nm; $C_{13}H_{14}N_2O_2S$ (230.4): Anal. calcd C 59.5, H 5.38, N 10.6; found: C 59.1, H 5.38, N 10.5.

4-[(*N*,*N*-Dimethylamino)(N-phenylamino)methylene]-3-methylisoxazol-5(4*H*)-one (9j): Colorless crystals, 65%, m.p. 220 °C; IR (KBr): $\tilde{\nu}$ = 1673, 1659 cm^{-1} (CO); ^1H NMR (200 MHz, $CDCl_3$): δ = 1.71 (s, 3H, CH_3), 3.04 (s, 6H, NCH_3), 6.97–7.34 (m, 5H, arom.); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 12.6, 40.9, 80.6, 120.1, 123.8, 129.3, 140.2, 157.1, 159.0, 172.2; UV: λ_{max} = 217, 273, 312 nm; $C_{13}H_{15}N_3O_2$: calcd 245.1178; found 245.1173 (HRMS).

4-[(*N*,*N*-Dimethylamino)(N-*p*-tolylamino)methylene]-3-methylisoxazol-5(4*H*)-one (9k): Colorless crystals, 68%, m.p. 208 °C; IR (KBr): $\tilde{\nu}$ = 1671, 1655 cm^{-1} (CO); ^1H NMR (200 MHz, $CDCl_3$): δ = 1.92 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 3.06 (s, 6H, NCH_3), 6.89–7.15 (m, 4H, arom.); ^{13}C NMR (50 MHz, [D$_6$]DMSO): δ = 13.0, 20.8, 41.1, 81.7, 120.7, 130.3, 134.9, 136.7, 157.9, 160.3, 173.7; UV: λ_{max} = 211, 273, 312 nm; $C_{14}H_{17}N_3O_2$: calcd 259.1321; found 259.1320 (HRMS).

(3-Methylthio)(3-*N*-phenylamino)-2-cyanoacrylonitrile (31): The compound was prepared according to the literature method [27]. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.26 (s, 3H, SCH_3), 7.27-7.47 (m, 5H, arom.), 8.22 (brs, 1H, NH); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.8, 57.5, 114.6, 124.2, 127.6, 129.7, 137.1, 172.5.

(3-Methylthio)(3-*N*-phenylamino)acrylonitrile (16): The compound was prepared according to the literature method [18]. A threefold set of ^{13}C NMR signals was observed due to (*E*)-, (*Z*)-, and imine forms. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.5, 15.1, 16.5, 64.5, 71.0, 114.5, 118.4, 119.3, 119.6, 122.6, 124.1, 124.4, 125.5, 125.8, 129.1, 129.5, 129.7, 138.3, 138.9, 148.9, 157.4, 158.8, 163.2.

Preparative FVT of 7e: Isoxazolone **7e** was pyrolyzed at 600 °C in the preparative FVT apparatus. The crude product obtained from the cold finger (48%) was shown by TLC to be one compound. ^1H and ^{13}C NMR, IR and MS data in comparison with the above data and the literature values [18] demonstrated that the product was **16**.

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